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STUDIES OF A SERIES OF HALO ALUMINUM, GALLIUM, AND INDIUM PHTHA--ETC(U)
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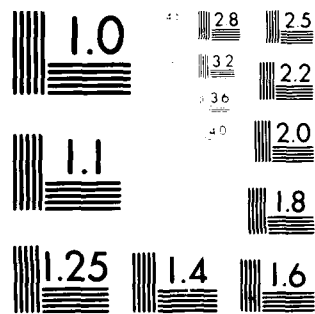
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Studies of a Series of Halo Aluminum, Gallium,
and Indium Phthalocyanines¹

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Abstract

Physical and chemical studies have been carried out on the series of phthalocyanines AlPcF, AlPcCl, AlPcBr, AlPcI, GaPcF, GaPcCl and InPcCl. It is concluded on the basis of mass spectroscopic, infrared, microscopic, x-ray, and other data collected in these studies that AlPcF and GaPcF are polymeric and have $(M-F)_x$ backbones. It is further concluded that the remaining compounds are non-polymeric.

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Introduction

In some of the very early work on phthalocyanines the compound $(AlPc)_2O$ was discovered.² From the findings in this work and work done later,³ it became clear that $(AlPc)_2O$ is a μ -oxo bridged compound, Figure 1.

Now a number of other such μ -oxo bridged compounds are known.³⁻⁷ Among these are $(MnPc)_2O \cdot 2py$,⁵ $[(Me_3SiO)_2MeSiO][GePcO]_2[SiMe(OSiMe_3)_2]$,⁶ $AlPcOSiPcOAlPc$,³ $[(MeSiO)_2MeSiO][SiPcO]_3[SiMe(OSiMe_3)_2]$,⁶ $Me_3SiO(SiPcO)_4SiMe_3$,⁷ and $[(Me_3SiO)_2MeSiO][SiPcO]_5[SiMe(OSiMe_3)_2]$,⁶ (so far no compounds of this type with more than five rings have been reported). The structures of two of these compounds $(MnPc)_2O \cdot 2py$ ⁸ and $[(Me_3SiO)_2MeSiO][SiPcO]_3[SiMe(OSiMe_3)_2]$ ⁹ have been determined.

In addition to these (relatively) low molecular weight μ -oxo bridged species, three μ -oxo bridged phthalocyanine polymers are known. These are $(SiPcO)_x$,¹⁰ $(GePcO)_x$,¹¹ and $(SnPcO)_x$.¹² The silicon polymer is quite stable and has attracted some notice because of this.¹³ Recently all three have drawn attention because they become conducting when oxidized with iodine.¹⁴

In view of this, other phthalocyanines which have similar polymeric structures are of interest. In the present paper, we report on procedures for making two such polymers and on some of the properties of these polymers. Their conductivities, when oxidized, are described elsewhere.¹⁵

Experimental

AlPcCl. Part of the AlPcCl used was made by a procedure reported earlier.¹⁶ Some of this was sublimed twice at 430°C under vacuum.

This gave a purple sublimate. Anal. Calcd for $C_{32}H_{16}N_8AlCl$: C, 66.85; H, 2.81; Al, 4.69; Cl, 6.17. Found: C, 66.56; H, 2.69; Al, 4.99; Cl, 5.94.

A modification of this procedure was found to be better. In this modified procedure a mixture of phthalonitrile (20g), aluminum trichloride (5.0g), and quinoline (distilled twice and then deoxygenated with nitrogen, 100mL) was refluxed for 30 min. The reaction mixture then was cooled to approximately 0°C and filtered. The solid thus isolated was washed with benzene, carbon tetrachloride, and acetone, and dried at ~110°C (10.7g).

For some of the work the compound was recrystallized twice from 1-chloronaphthalene.

AlPcF.¹⁷ A mixture of AlPcCl (2.5g), concentrated ammonium hydroxide (50mL), and pyridine (25mL) was refluxed for 7h. The resulting solid was filtered and the filter cake was washed with pyridine, concentrated ammonium hydroxide, and hot water. It was then dried at 110°C (2.3g).

A portion of this product, $AlPcOH \cdot H_2O^3$, (2.1g) was evaporated to dryness on a steam bath with two separate portions of 48% hydrofluoric acid (~18mL each time). The resulting solid was washed with water, methanol, pyridine, and acetone and dried at 110°C (1.9g). A portion of this was heated to 540°C under vacuum. The product was vacuum sublimed three times, the final sublimation being carried out at 540°C. This gave a blue, velvety sublimate. Anal. Calcd for $C_{32}H_{16}N_8AlF$: C, 68.82; H, 2.89; Al, 4.83, F, 3.40. Found: C, 69.05; H, 3.01; Al, 5.01; F, 3.26.

This compound was found to be quite insoluble in a variety of organic solvents.

AlPcBr.¹⁸ A mixture of $\text{AlPcOH} \cdot x\text{H}_2\text{O}$ (5.0g), tri-*n*-hexylsilanol (7.0mL), and toluene (100mL) was refluxed for 8 h. The reaction mixture was filtered while hot and evaporated to dryness (6.2g). The product was recrystallized from *n*-hexane.

A portion of this product, assumed to be $\text{AlPcOSi}(\text{C}_6\text{H}_{13})_3$,¹⁹ (0.40g) was suspended in benzene (100mL) and hydrogen bromide was slowly bubbled into the mixture for 15 min. The solid was filtered off, washed with benzene, and briefly digested in refluxing bromonaphthalene (10mL). The resultant was recovered by filtration, recrystallized from bromonaphthalene, washed with benzene containing a small amount of hydrogen bromide, and vacuum dried at 100°C. This gave relatively large, red-reflecting, green-transmitting crystals. Anal. Calcd for $\text{C}_{32}\text{H}_{16}\text{N}_8\text{AlBr}$: C, 62.05; H, 2.60; Al, 4.36; Br, 12.90. Found: C, 61.79; H, 2.70, Al, 4.13; Br, 13.12.

AlPcI. Hydrogen iodide was slowly bubbled into a suspension of $\text{AlPcOSi}(\text{C}_6\text{H}_{13})_3$ (0.20g) in benzene (35mL) for 15 min. The reaction product was separated by centrifugation and dried with a rotary evaporator. Portions of it were sublimed at 420°C under vacuum. (Small scale sublimations were used in the sublimation step since larger scale ones gave poor yields.) The mass spectrum of this product showed the expected arrays but none for other phthalocyanines or for hydrogen iodide.

GaPcCl. This compound was prepared, as it had been earlier,²¹ by a template reaction. Gallium trichloride and 1,3-diiminoisoindoline were used as reactants. A portion of the product was sublimed at 430°C under vacuum. This gave a purple sublimate. Anal. Calcd for $\text{C}_{32}\text{H}_{16}\text{N}_8\text{GaCl}$:

C, 62.22; H, 2.61; Ga, 11.29; Cl, 5.74. Found: C, 62.44; H, 2.73; Ga, 11.43; Cl, 5.79.

A procedure similar to a known alternative one for the compound²² was found to be more satisfactory. In this procedure a mixture of phthalonitrile (20g), gallium trichloride (5.5g), and doubly distilled, deoxygenated quinoline (100mL) was refluxed for 1 h (particular attention was paid to excluding water during this step). After being cooled to approximately 0°C, the reaction mixture was filtered. The product was washed with toluene and methanol and dried at ~110°C (9.4g).

GaPcF. A mixture of GaPcCl (1.5g), concentrated ammonium hydroxide (35mL), and pyridine (35mL) was refluxed for 20 h. The reaction product was filtered and the solid was washed with water, methanol, and acetone, and dried at 100°C (1.4g).

A portion of this product, assumed to be GaPcOH·xH₂O, (0.92g) was evaporated to dryness on a steam bath with two separate portions of 48% hydrofluoric acid (15-20mL each). The resulting solid was washed with water, methanol, pyridine, and acetone and dried at 110°C (0.89g). A portion of this was heated to 460°C under vacuum and the product was sublimed at this temperature under vacuum. This gave a purple sublimate.

Anal. Calcd for C₃₂H₁₆N₈GaF: C, 63.93; H, 2.68; Ga, 11.60; F, 3.16. Found: C, 63.79; H, 2.67; Ga, 11.52; F, 2.98.

This fluoride was found to be relatively insoluble in a variety of organic solvents. However, it was found that it could be recrystallized from 1-chloronaphthalene and quinoline.

InPcCl. This compound was prepared by a method similar to one which has been described.²³ A portion of the InPcCl thus obtained was vacuum sublimed twice, the second sublimation being carried out at 370°C.

The resulting sublimate was purple. Anal. Calcd for $C_{32}H_{16}N_8InCl$: C, 57.99; H, 2.43; In, 17.32; Cl, 5.35. Found: C, 58.12; N, 2.61; In, 17.46; Cl, 5.59.

A second procedure similar to another procedure which has been described for this compound²⁴ was found to be superior. In this procedure a mixture of phthalonitrile (10g), indium trichloride (3.5g), and doubly distilled, deoxygenated quinoline (100mL) was refluxed for 1 h (particular care was taken to exclude water during this step). The reaction mixture was then cooled to approximately 0°C. The product was isolated by filtration and then was washed with methanol, toluene, and acetone, and dried at ~110°C (6.3g).

Contrary to earlier reports^{21,25} it was found that concentrated sulfuric acid demetallates $InPcCl$. It was further found that a strong aqueous sulfuric acid solution (9:1) does not demetallate nor hydrolyze the compound and that refluxing dilute sodium hydroxide (2.5M) and refluxing concentrated ammonium hydroxide-pyridine (2:1) solutions do not hydrolyze it.

Sampling Techniques and Instrumentation. The infrared studies were carried out on films of the compounds deposited by sublimation on cesium bromide or cesium iodide plates. These studies were done with a Beckman IR-12 spectrometer. The electron microscopy studies were done with Japan Electron Optics JEM-6A and Hitachi HU-11A microscopes. Some of the x-ray powder studies were performed on samples of the compounds which had been deposited on glass plates by vacuum sublimation. Others were performed on samples which had been deposited on glass plates by dropping hexane-mineral oil suspensions of the samples on the plates and allowing the suspensions to evaporate down. These studies were carried out with a General Electric XRD-5 spectrometer using cobalt radiation and an iron

filter. The single crystal x-ray studies were carried out with a Weissenberg camera. The mass spectroscopy work was done with a Varian M-66 instrument. It was operated at 70 eV.

AlPcF and GaPcF Crystal Growth. Crystals of AlPcF were grown by sublimation in the 400-500°C range under vacuum and by sublimation at above 500°C under a flow of helium or argon. Crystals of GaPcF were similarly grown by vacuum sublimation at high temperatures and by sublimation under a flow of helium at high temperatures, typically 500-540°C.

Results and Discussion

Physical Studies. A variety of studies were carried out on the compounds. Among the data collected in these studies were mass spectral data on the four aluminum halides, Table I.²⁶ An important point with regard to these data is the absence of a significant array for the AlPcF^+ ion in the spectrum of the fluoride (even though relatively high probe temperatures were used with this compound). Another important point is the presence of an array for this ion in the spectrum of the pyridine-washed precursor of the fluoride (this species is probably HALPcF_2 or a related compound) and, fleetingly, an array for it in the spectrum of the bromide studied.

Infrared data were also collected on some of the compounds in the region between 200 and 4000 cm^{-1} .^{27,28} As expected, the spectra of these compounds show a great many similarities. Of most importance to the present work are the bands in these spectra associated with the metal-halogen stretching vibrations. Comparisons of the spectra suggest the assignments listed in Table II. Particularly noteworthy with regard to these is the substantial broadness of the bands assigned to the Al-F and Ga-F vibrations.

Information on the habit of the crystals of the two fluorides was acquired as well. It was found that the AlPcF crystals formed by vacuum sublimation were very small and needle-like, Figure 2. Likewise it was found that the crystals of this compound formed by atmospheric-pressure inert-gas sublimation were small and needle-like. The crystals of GaPcF obtained by vacuum sublimation were observed to be somewhat larger than those of AlPcF obtained by this technique although they too were very small. In contrast, some of the crystals of GaPcF obtained by atmospheric-pressure, helium-atmosphere sublimation were found to be considerably larger, i.e., up to 2mm in length.

In the process of carrying out the electron microscopy work on the fluorides, several micrographs of sublimed AlPcF crystals were obtained which showed lattice images. The lines in these images are spaced by about 13 to 15Å and run parallel to the long axes of the crystals.

Figure 3.

In addition to these data on the fluorides, data on the behavior of their crystals in polarized light was collected. It was found that bundles of the vacuum sublimed AlPcF crystals were blue-green when observed with light polarized perpendicular to the long axis of the crystals and that bundles of the vacuum sublimed GaPcF crystals were blue when observed under these conditions. It was further found that, when observed with light polarized parallel to their long axes, both kinds of crystals were nearly colorless. As is to be expected in view of this, the ribbon-like helium-atmosphere sublimed GaPcF crystals, when resting on their flat faces, were found to exhibit a blue color with light polarized perpendicular to their long axis and almost no color with light polarized parallel to this axis.

X-ray data on the fluorides were also obtained. Powder pattern data for sublimate of AlPcF, where many of the crystals were at an angle

to the supporting plate, were found to show a strong reflection at 3.66\AA and a somewhat less strong one at 3.55\AA . In contrast, powder data for a mull of sublimed AlPcF where most of the crystals were parallel to the supporting plate, were found to almost completely lack these reflections. Similarly, the powder data for a GaPcF sublimate, where again many of the crystals were at an angle to the supporting plate, were found to show a strong reflection at 3.86\AA and a less strong one at 3.70\AA , and the corresponding data for a mull of sublimed GaPcF, where, as in the like AlPcF case, most of the crystals were parallel to the plate, were found to be deficient in these reflections.

Data from a rotation photograph of a helium-sublimed single crystal of GaPcF suggest that one of its crystallographic axes was approximately parallel to its long dimension and that the length of this axis was 3.89\AA . Corresponding data from zero level photographs of the crystal tentatively suggest that it had tetragonal symmetry but those from first level photographs do not bear this out nor suggest an alternative symmetry.

The Fluorides. Taken together the available data on AlPcF and GaPcF leave little doubt as to the nature of these compounds. Thus the low solubility and low volatility of the aluminum compound and the low solubility of the gallium compound suggest that both are polymeric. (The fact that both sublime at elevated temperatures is understandable in terms of a depolymerization process involving MPcF monomers or $(\text{MPcF})_x$ oligomers.) Similarly, the absence or near absence of an array for the AlPcF^+ ion in the mass spectrum of AlPcF and the (fleeting) presence of an array for it in the spectrum of AlPcBr containing AlPcF as a minor impurity (where the AlPcF likely occurs as a monomer or as a fluoride-bridged oligomer, e.g., AlPcFAlPcBr) suggests that this compound (except when highly dilute) is polymeric.

The breadth of the infrared band identified as the Al-F bond in AlPcF further suggests that this compound has an $(\text{Al-F})_x$ backbone. This in turn implies that the polymer is made up of stacked AlPcF units, Figure 4. Correspondingly the shape of the band identified as the Ga-F bond in GaPcF indicates that this compound has a $(\text{Ga-F})_x$ backbone and that it too has a stacked-ring structure.³⁰

The occurrence of lattice images in micrographs of AlPcF and the spacing of the lines in these images by an amount which approximately corresponds to the van der Waals width of the phthalocyanine ring³¹ supports the structural arrangement suggested by the infrared data.³² In addition, the orientation of the lines in these images suggests that the chains are packed parallel to the long axes of the crystals. Because of the similarity of AlPcF and GaPcF, these lattice image data also suggest that in GaPcF the chains are packed parallel to the long axes of the crystals.

Further support for the postulated structure of AlPcF is found in the existence and orientation of the strong blue-to-colorless dichroism characteristic of its crystals. Likewise support for the postulated structure for GaPcF is found in the existence and orientation of the dichroism of its crystals.

The almost complete absence of 3.55 and 3.66 \AA reflections in the x-ray powder data for AlPcF when the crystallites are largely oriented so that their long axes are parallel to the mounting plate suggests that the ring-ring separation in this compound is in the 3.5 to 4.0 \AA range. In addition, the relative intensities of the two lines when observed leads to speculation that the ring-ring separation is 3.66 \AA . Similarly, the powder data on GaPcF suggest that in this compound the ring-ring separation is also in the 3.5 to 4.0 \AA range and that it may be 3.86 \AA . Support for the

3.86Å value is provided by the Weissenberg data on this compound. That spacings in the 3.5 to 4.0Å range are indicated for GaPcF and AlPcF is not surprising because the sums of the pertinent radii are in this range, i.e., $2(0.535_{\text{Al}} + 1.285_{\text{F}}) = 3.64_{\text{Al-F-Al}}^{\circ}\text{Å}$ and $2(0.620_{\text{Ga}} + 1.285_{\text{F}}) = 3.81_{\text{Ga-F-Ga}}^{\circ}\text{Å}$.³³ (The van der Waals thickness of the ring is not a governing factor because it is slightly below 3.5Å, i.e., about 3.3 to 3.4Å.³⁴)

In sum, then, it is clear that these compounds are polymeric, that the molecules in them have $(\text{M-F})_x$ backbones, and that these backbones are surrounded by a sheath of phthalocyanine rings stacked face-to-face. In addition, it is apparent that these molecules are linear and are packed parallel to the long axes of the crystals. Further, it seems likely that the ring-ring separation is 3.66Å in the aluminum compound and 3.86Å in the gallium compound.

The fact that these fluorides should have such structures is not surprising because they are isoelectronic with the stacked-ring polymers $(\text{SiPcO})_x$ and $(\text{GaPcO})_x$. In addition, many bridged systems in which the bridging atoms are fluorine atoms are known.

The strength of the bonding in the $(\text{M-F})_x$ backbones of these polymers probably is quite substantial. Whether or not this is the case, $d_{\pi}-P_{\pi}$ bonding may well contribute importantly to the bonding in them because it seems likely that these backbones have symmetrical, linear M-F-M bridges.

A particularly useful property of these compounds is their volatility. This not only permits the purification of them by sublimation, but also opens a possible route to well-ordered, good-sized single crystals of them. Such crystals would be valuable for a variety of reasons.

Because these two compounds are stacked-ring polymers, it appears highly likely that other fluoride-bridged phthalocyanine polymers will

be found. Further, it seems probable that polymers of this type with other ring systems will also be found.

The Other Halides. The other compounds dealt with in this paper, i.e., the aluminum chloride, bromide, and iodide and the gallium and indium chlorides appear, on the basis of what is known, to be ordinary square-pyramidal phthalocyanine complexes. Thus, the infrared bands assigned to the M-X stretching vibrations in AlPcCl , and AlPcBr are reasonably narrow.

An interesting feature of the mass spectra of AlPcCl , AlPcBr , and AlPcI is the pattern of the intensities of the AlPcX^+ and AlPc^+ ion arrays. This suggests that the strength of the Al-X bond decreases, as expected, as the size of the halogen increases.

The great resistance of InPcCl to hydrolysis is striking in view of the relative lack of resistance of AlPcCl and GaPcCl to hydrolysis. However, it does find a parallel in the behavior of chloroindium octa-ethylporphyrin.³⁵

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Table I
Mass Spectroscopy Data

	Purification	Probe Temperature	Pc ⁺	AlPc ⁺	AlPcX ⁺	Other Ions
AlPcF	sublimed	450-480°C	0	0	^a	
AlPcCl	recrystallized	350	0	30	100	
AlPcBr	recrystallized ^b	350	0	139	100	AlPcF ⁺ , AlPcCl ⁺
AlPcI	sublimed	350	0	305	100	
AlPcF precursor	-	400	0	0	100	HF ⁺

^a small or absent

^b This sample apparently contained very small AlPcF and AlPcCl impurities.

Table II
M-X Stretching Vibrations^a
cm⁻¹

	AlPcX	GaPcX
F	550 m, b ^b	517 w, b ^b
Cl	440 m ^c	
Br	397 m	
I	<200	

^a m = medium w = weak b = broad

^b These bands are overlapped by other bands.

^c It is uncertain whether the absorption at 433 cm⁻¹ reported by Starke and Hamann²⁷ corresponds to this absorption.

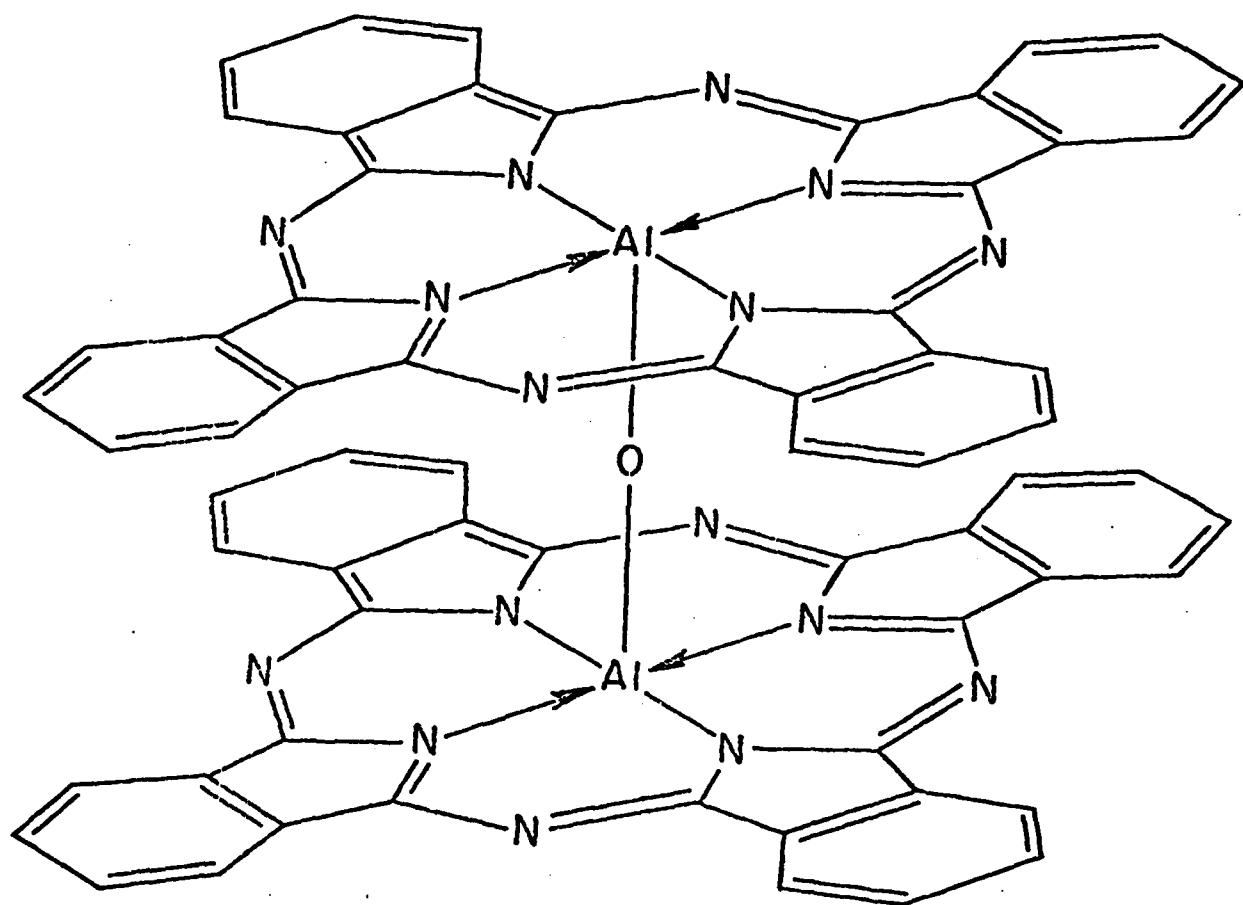
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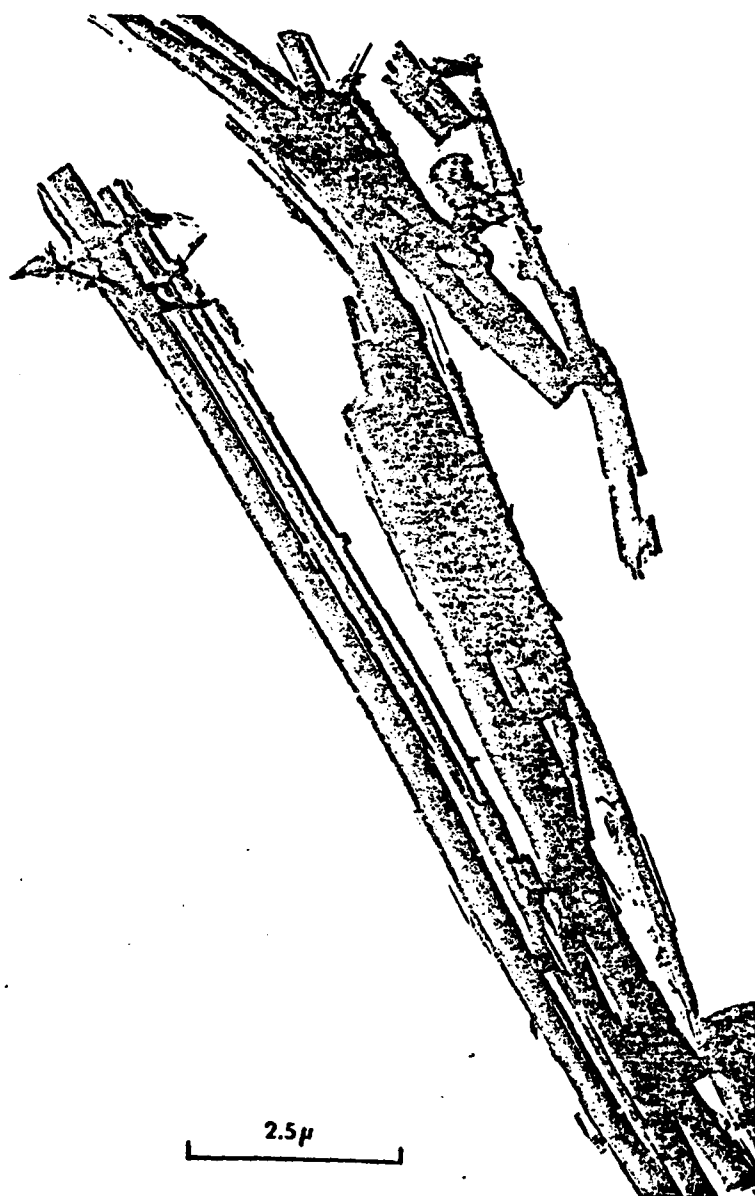
Figure 1. The structure of $(\text{AlPc})_2\text{O}$

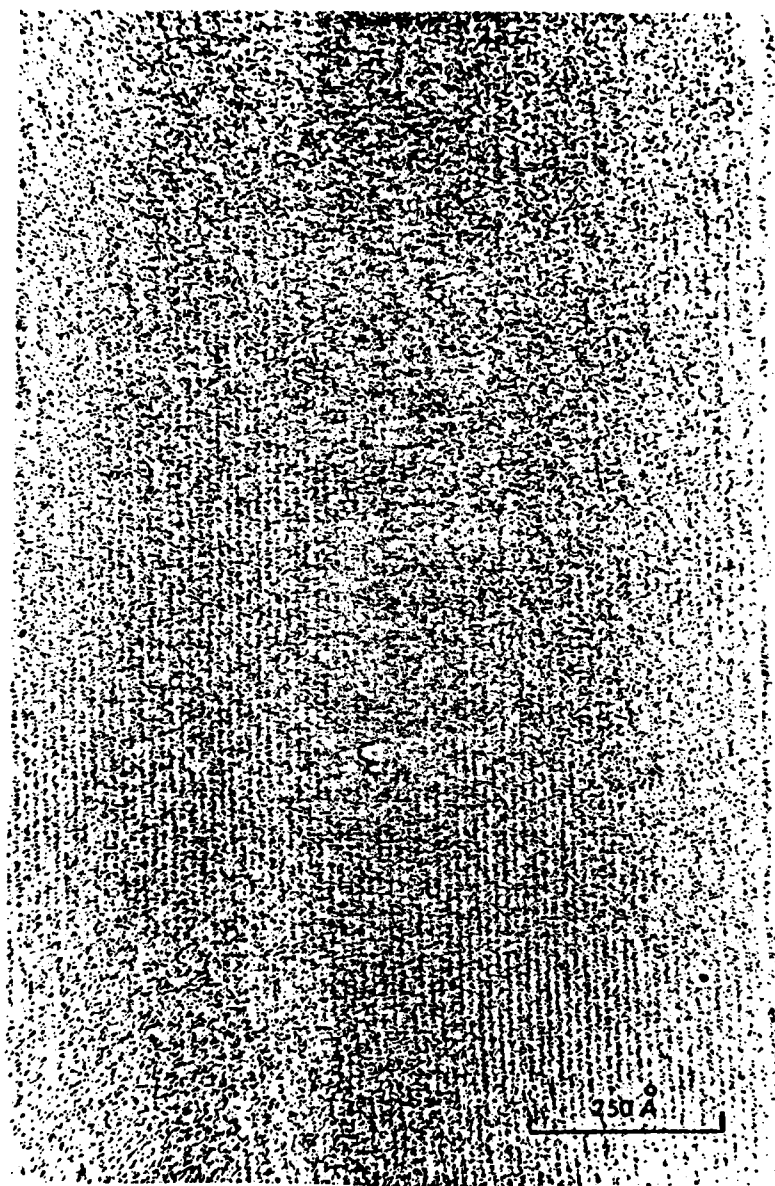
Figure 2. Crystals of sublimed AlPcF

Figure 3. Lattice image of a AlPcF crystal

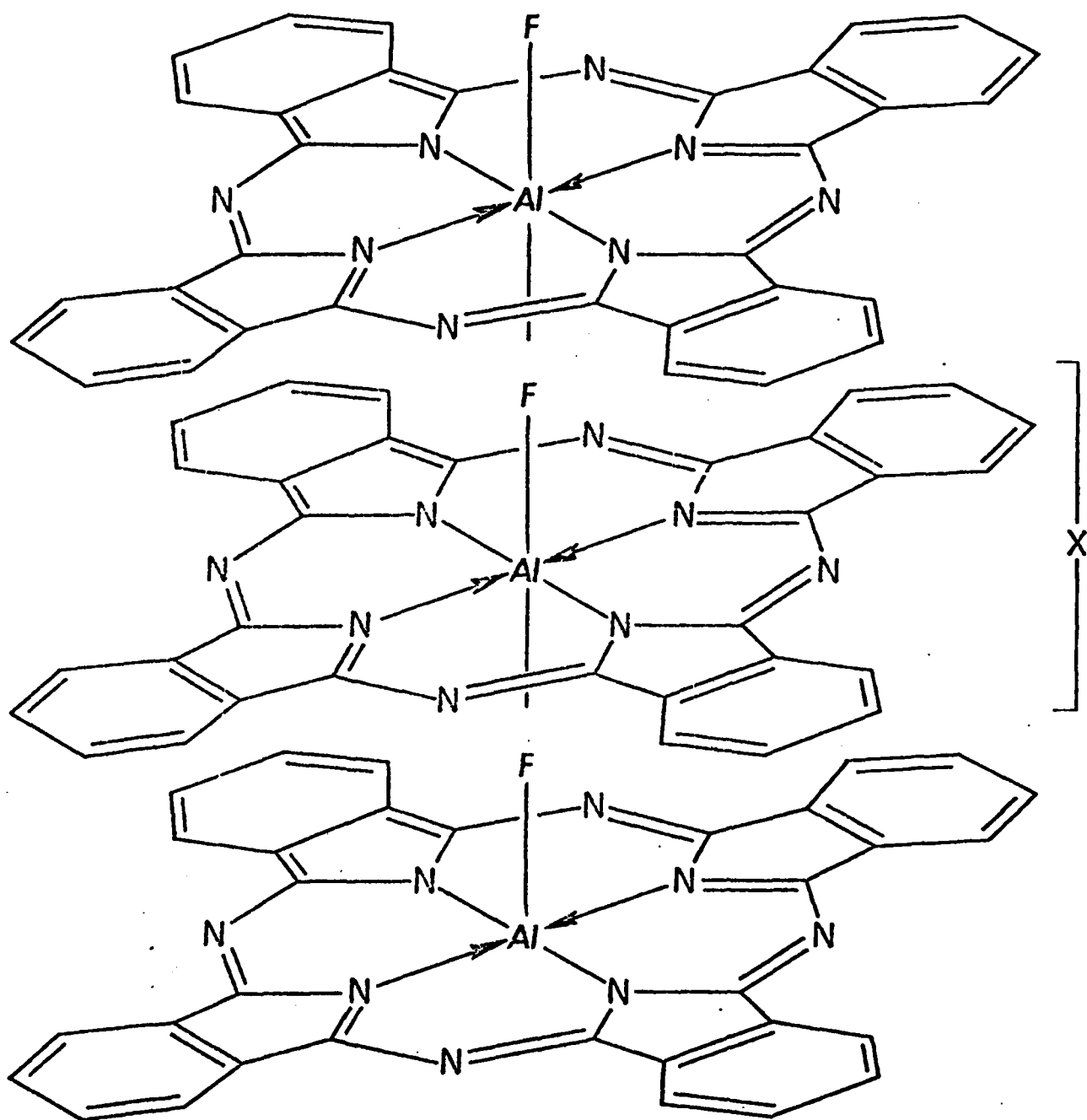
Figure 4. The structure of $(\text{AlPcF})_x$







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